



LANSCCE DIVISION RESEARCH REVIEW

Phonon Thermodynamics of Transition Metals and Alloys

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Understanding the fundamental thermodynamics of pure metals and alloys allows for better prediction of their behavior for everyday applications. The knowledge of the thermodynamics of a metallic alloy tells us the structural arrangements of atoms that are the most stable at a given composition and temperature. This is crucial information for materials engineering if one is to design safer and more reliable mechanical systems (from cars to the space shuttle), faster electronic devices, or magnetic systems with larger information-storage capabilities. This knowledge about materials structures is summarized in so-called “phase diagrams.”

Phase diagrams can be derived from knowledge of the underlying thermodynamic free energy of materials, and in recent years this free-energy information has been obtained from quantum-mechanical computer calculations. The implementation of these calculations is, however, not yet fully settled. An important, but hard to theoretically assess, contribution to the thermodynamics of metallic systems is the vibrational entropy contribution, or phonon entropy.

The vibrational entropy of an ensemble of atoms is the degree of disorder, or, as Ludwig Boltzmann showed in the frame of statistical mechanics, the number of states accessible through the vibrations of its constituent atoms. It has been experimentally demonstrated in the past decade that vibrational entropy can account for a large portion of the entropy difference that drives solid-solid phase transitions.¹ The most powerful way to determine the vibrational entropy of a crystal is to measure its phonon density of states (DOS). Phonons are the normal modes of atomic vibrations of a crystal lattice, and the PHAROS (phased rotor spectrometer) inelastic neutron spectrometer at the Lujan Center is well-suited for measuring the energy spectra of phonons in materials.² With accurate spectra of phonon energies, it is possible to obtain the partition function that contains all information about phonon thermodynamics.^{2,3} This is useful information by itself, but with further modeling of the atom vibrations, we can also understand why the phonon DOS changes with the structure of the material.

Experiments

The entropy of one family of phase transitions, called “martensitic transformations”, can be entirely vibrational in origin. Because this transformation occurs by cooperative and well-organized shears of the crystal, the disorder of the atomic configurations does not significantly change. By measuring the phonon DOS in the alloy $\text{Fe}_{71}\text{Ni}_{29}$ undergoing the face-centered cubic (fcc) to body-centered cubic (bcc) martensitic transformation, we were able to determine the vibrational entropy source of this transformation and study the interatomic forces that are responsible for this change in atom vibrations. The phonon DOS of a $\text{Fe}_{71}\text{Ni}_{29}$ polycrystalline sample was measured as the sample underwent its fcc-to-bcc transformation as the sample was cooled from room temperature to 80 K. The low-temperature bcc martensite phase does not transform back into fcc austenite, unless one heats it to at least 400 °C. Both the austenite and the martensite were therefore measured at room temperature to allow for direct comparison of their phonon DOS curves.

In a separate experiment, we studied anomalies in the vibrational spectrum of nickel metal at high temperature. In particular, we sought to measure the degree of anharmonicity of its interatomic potential. We measured inelastic neutron scattering (INS) spectra from phonons in pure nickel from a polycrystalline sample mounted inside a vacuum furnace designed for neutron-scattering experiments. The spectra were acquired up to the temperature of 1050 °C. All INS spectra were measured on the PHAROS spectrometer at LANSCE.

Results

■ Martensitic Transition in $\text{Fe}_{71}\text{Ni}_{29}$

Before the measurements on PHAROS, we checked the martensitic phase transition in samples of alloy by measuring the austenite (fcc) phase-fraction evolution as function of temperature by conventional x-ray diffractometry. A reduction of the neutron-scattering-data-produced phonon DOS curves for the fcc and bcc phases is presented in Figure 1. Also shown in this figure is the DOS of fcc $\text{Fe}_{70}\text{Ni}_{30}$ obtained by Brockhouse *et al.*⁴ by fitting phonon dispersions to a Born/von Karman model. The broadening of our DOS curves is caused by the inherent energy resolution of the PHAROS instrument, but after accounting for this broadening, we see excellent agreement between our result for direct measurement of the phonon DOS and that of Brockhouse, obtained from dispersion curves. The positions of van Hove singularities as well as the cutoff maximum energy are in clear agreement, and the low-energy acoustic regions are virtually identical.

The most important change in the DOS between the fcc and bcc phases is the shift of the phonon mode distribution towards higher energies in the lower-temperature bcc phase. In particular, the cutoff energy is raised by 2 meV in the bcc compared to the fcc phase. This shift indicates an overall stiffening of interatomic force-constants in the fcc phase. This stiffening results in a net decrease in the vibrational entropy of the alloy because the atoms do not

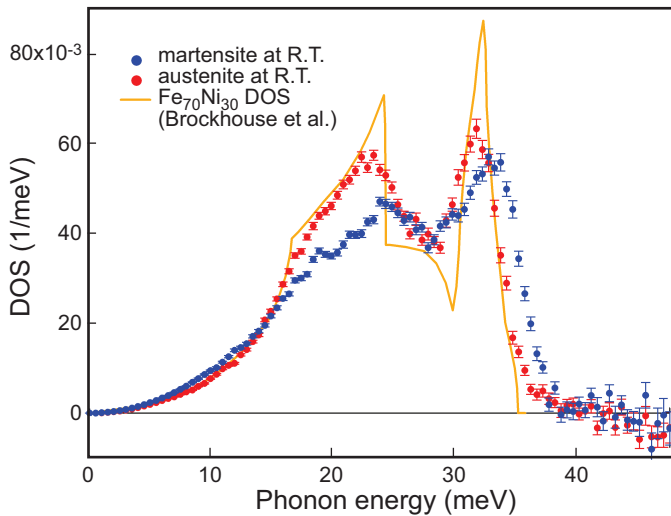


Figure 1. Phonon DOS curves for $\text{Fe}_{71}\text{Ni}_{29}$ austenite (fcc) and martensite (bcc) measured at room temperature, and DOS curve from Born/von Karman fit to dispersions of $\text{Fe}_{70}\text{Ni}_{30}$ (Brockhouse *et al.*⁴).

move as far at a given temperature. The difference in vibrational entropy between these two phases, $\Delta S_{vib}^{fcc \rightarrow bcc} = -0.13 k_B/\text{atom}$, is significant and is representative of this kind of martensitic transformation.

At present, we are modeling the lattice dynamics to test the likely source of this entropy difference in terms of the interatomic forces. As part of this effort, we are studying the coherent scattering information contained in the scattering function $S(|\vec{Q}|, E)$. Plots of $S(|\vec{Q}|, E)$ for both the fcc and bcc phases are presented in Figure 2. First notice the bright Bragg diffractions at zero energy transfer, which show the samples to be primarily fcc and bcc phase. The streaks originating from the Bragg diffractions are orientation-averaged phonon dispersions. These dispersions provide us with more detailed information about the interatomic potentials and force-constants in the material. By comparing the data (Figure 2c) to the results of a simulated phonon scattering (Figure 2), we are evaluating the interatomic force-constants for the Born/von Karman model of lattice dynamics.

■ High-Temperature Thermodynamics of Pure Nickel Metal

The number of phonons increases with temperature, increasing the amount of inelastic phonon scattering. Although phonon measurements might seem easier at elevated temperature, this is in fact a challenging task, owing to the background caused by the furnace itself. Thanks to the specially designed PHAROS furnace, we were able to measure INS spectra from nickel at temperatures reaching 1050 °C. Results are presented in Figure 3, as scattering angle-integrated $S(E)$ curves at temperatures of 25 °C, 700 °C, and 1050 °C. The signal from the furnace has been subtracted. Our 25 °C data are in good agreement with a previous measurement of the nickel phonon DOS by Brockhouse *et al.*⁵ and our 700 °C data are consistent with the 400 °C result of these authors. One can observe a clear softening (shift to lower energies) of the curves, and notably on the sharp features such as the longitudinal phonon peak (from 33 meV at room temperature to 30 meV at 1050 °C). This shift is accompanied by a broadening of the features, as is obvious on the longitudinal peak. From our preliminary analysis of the high-temperature nickel modes behavior, it appears that the phonon softening might follow a nonlinear behavior, with a stronger softening happening below 700 °C, followed by relatively weak softening at higher temperatures.

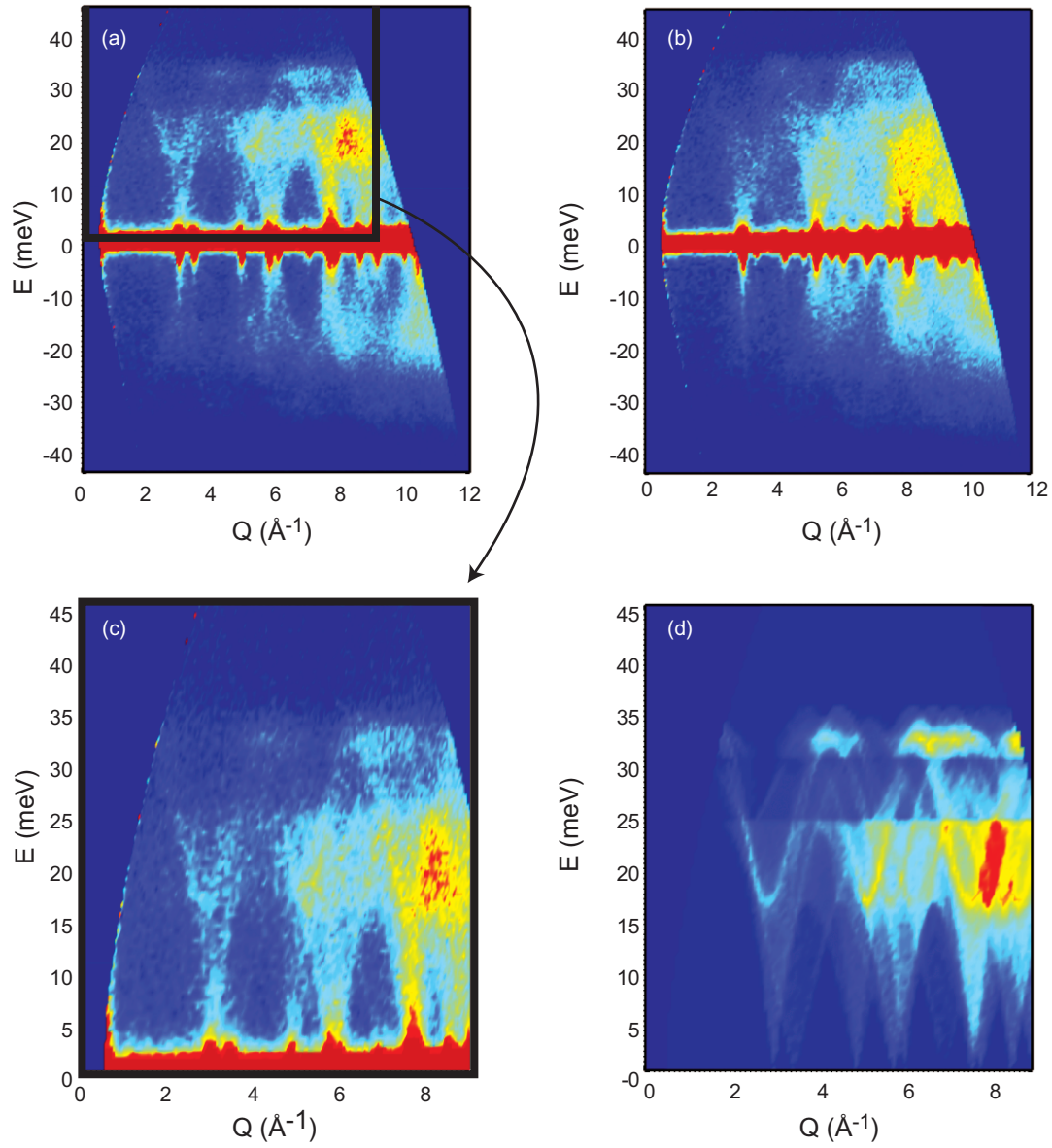


Figure 2. (a) $S(|Q|, E)$ for $\text{Fe}_{71}\text{Ni}_{29}$ fcc phase. (b) $S(|Q|, E)$ for $\text{Fe}_{71}\text{Ni}_{29}$ bcc phase. (c) Magnified view of inset in (a). (d) Calculated $S(|Q|, E)$ for fcc phase from Born/von Karman lattice-dynamics model corresponding to region (c).

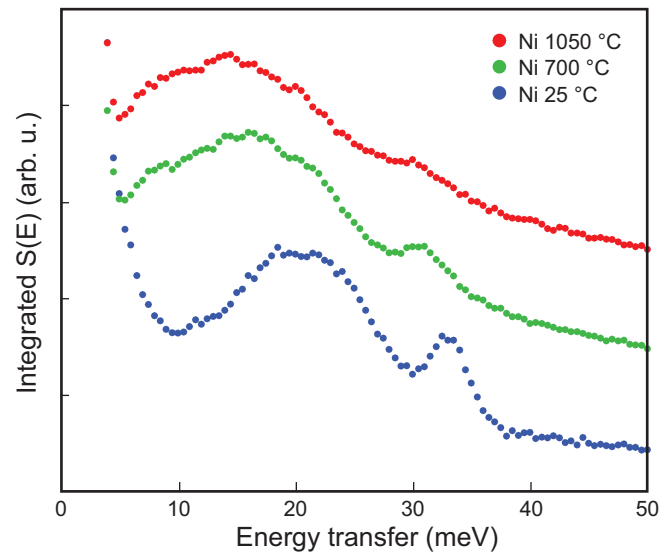


Figure 3. Integrated phonon scattering function $S(E)$ for pure nickel at 25 °C, 700 °C, and 1050 °C measured on the PHAROS spectrometer at the Lujan Center.

Conclusion

The thermodynamic partition function governs all thermodynamics of materials. It can be determined from the spectrum of excitations in materials. For phonons and magnetic excitations, these spectra can be measured with INS using instruments such as PHAROS at the Lujan Center. Such measurements identified the phonon entropy of the martensitic phase transition in $\text{Fe}_{71}\text{Ni}_{29}$ at low temperatures. Beyond the energy spectra, detailed information on the momentum transfer is available in data from PHAROS, and this information enables detailed modeling of the lattice dynamics. We are using this information to identify the origin of the entropy of the martensitic transition in terms of the interatomic forces. For the thermodynamics of high temperatures, data were acquired successfully on the softening of the phonons in nickel metal and the lattice-dynamics behavior at high temperatures is currently under analysis.

Acknowledgments

The authors would like to acknowledge the support from the U.S. Department of Energy Office of Basic Energy Sciences.

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LA-UR-05-2861

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